

Thin Films of Polypyrrole on Particulate Aluminum

1

*CHRISTOPHER VETTER, XIAONING QI,
SUBRAMANYAM V. KASISOMAYAJULA, AND
VICTORIA JOHNSTON GELLING*

DEPARTMENT OF COATINGS
AND POLYMERIC MATERIALS

NORTH DAKOTA STATE UNIVERSITY,
1735 NDSU RESEARCH PARK DRIVE
FARGO, ND 58105

V.J.Gelling@ndsu.edu

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE FEB 2009		2. REPORT TYPE		3. DATES COVERED 00-00-2009 to 00-00-2009	
4. TITLE AND SUBTITLE Thin Films of Polypyrrole on Particulate Aluminum				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) North Dakota State University, Department of Coatings and Polymeric Materials, 1735 NDSU Research Park Drive, Fargo, ND, 58105				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES 2009 U.S. Army Corrosion Summit, 3-5 Feb, Clearwater Beach, FL					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 21	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

Acknowledgments

2

Funding:

- Army (ARL), Contract No. W911NF-04-2-0029

Graduate Students

Xiaoning Qi
Christopher Vetter
Subramanyam V Kasi Somayajula
Kiran Bhat Kashi
Drew Pavlacky

Undergraduate Students

Emily Johnson
Jeffrey Garty

Post-Doctoral Associate

Dr. Maocheng Yan

Laboratory Assistant

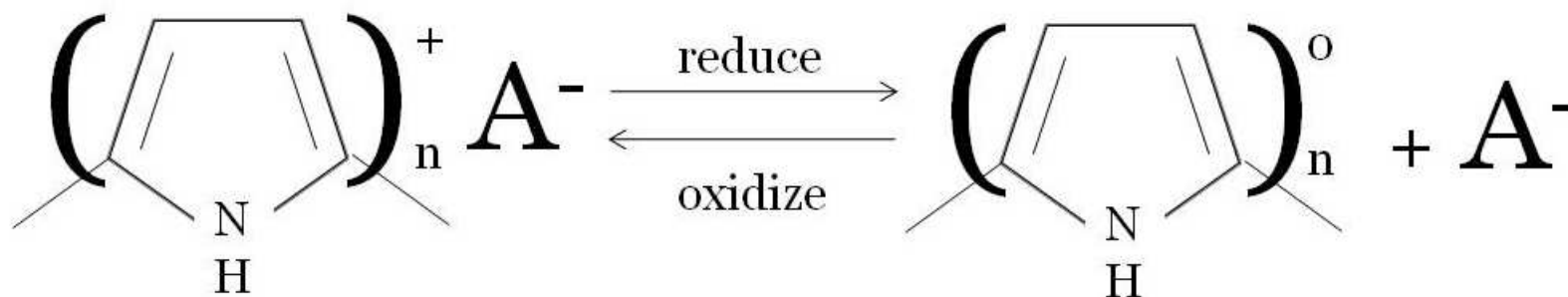
Kenneth Croes



Why Conducting Polymers?

3

- Perhaps act as “Smart Coating”
 - Release of Corrosion Inhibiting Anions
- Mixed Potential between surface and ECP
- Perhaps acts as an oxidant to form passive layer



Why Polypyrrole/Flake?

4

Polypyrrole

- ✗ Poor mechanical properties
- ✗ Poor adhesion
- ✗ Solubility issues
- ✗ Continuous layer needed

Polypyrrole Coated Flake

- ✗ Easy coating incorporation
- ✗ Less quantity of conducting polymer required
- ✗ Solubility is not an issue

Synthesis

5

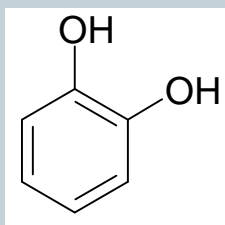
Synthesis Details

Ex #	Al Flake (g)	Pyrrole (ml)	Catechol (g)	$(\text{NH}_4)_2\text{S}_2\text{O}_8$ (g)	H_2O (ml)
1	50	11.5	18.2	37.7	1650
2	50	11.5		37.7	1650

Al flake paste combined with:

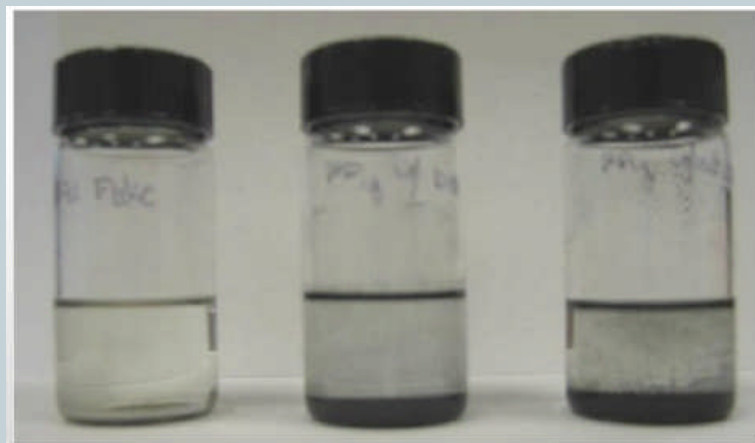
- DI water
- Catechol ($\text{C}_6\text{H}_6\text{O}_2$)
- $(\text{NH}_4)_2\text{S}_2\text{O}_8$
- Pyrrole monomer

Vacuum filtration & paste dried overnight, then ground using mortar and pestle and passed through a sieve with 150 μm pore size



Catechol

Density Test



As Received

Ex 1

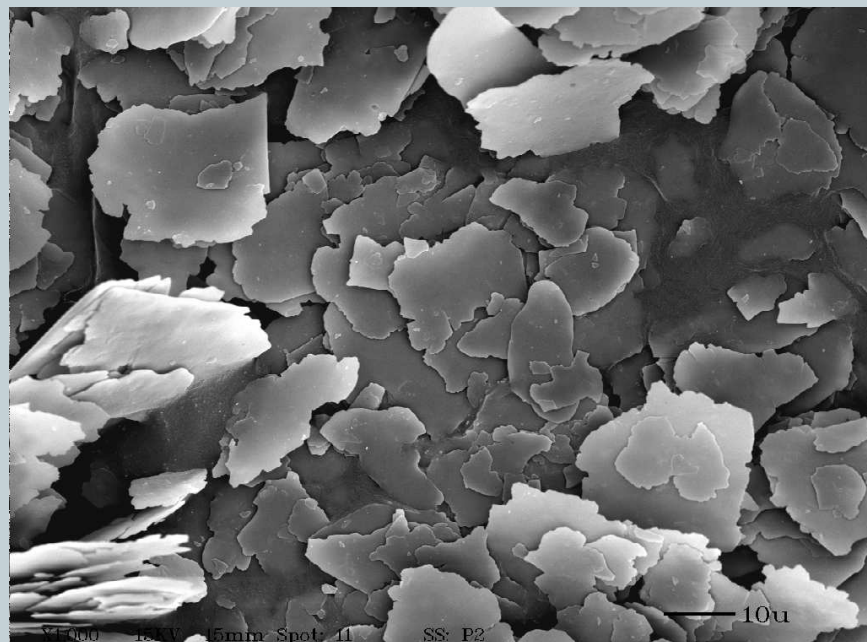
Ex 2

Tetrachloroethylene (1.622 g/cm³)
Plain Aluminum Flake (2.70 g/cm³)
Polypyrrole (0.967 g/cm³)

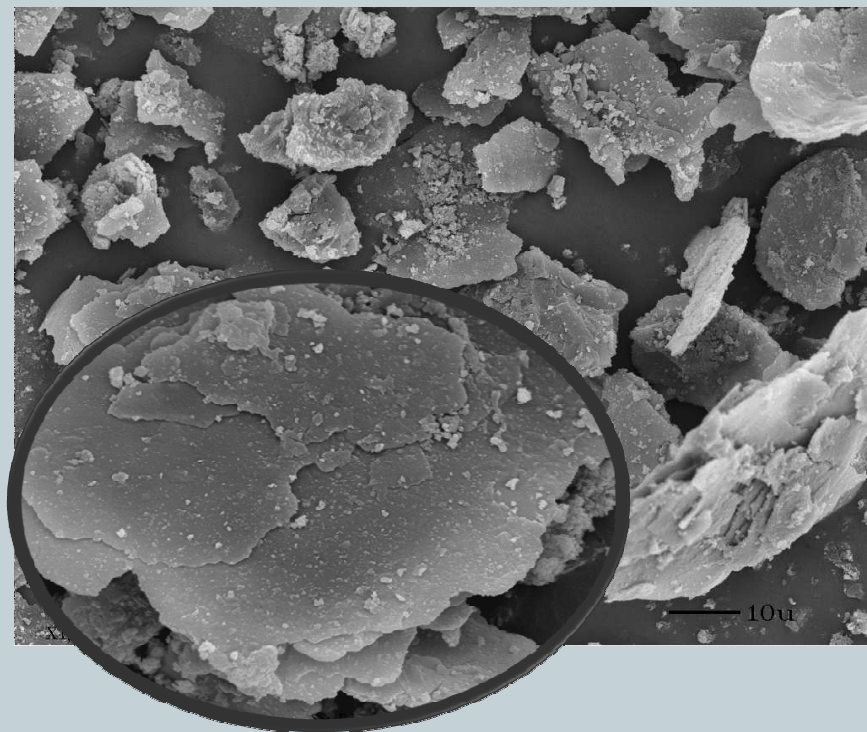
SEM

6

**As Received
Aluminum Flake**



**PPy (Catechol)
Ex #1**

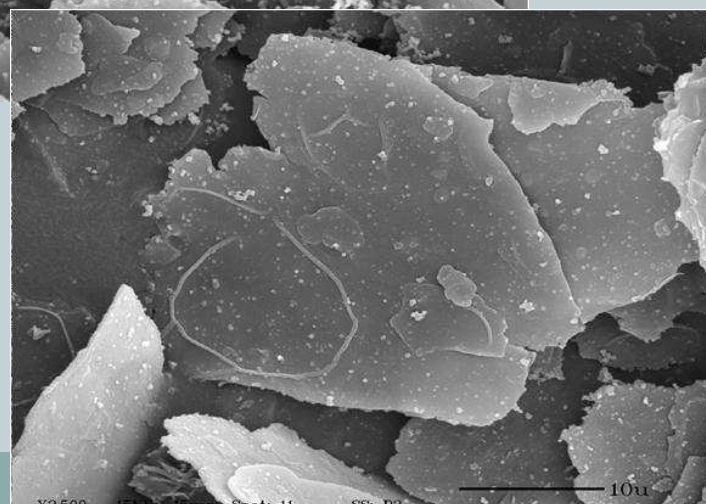
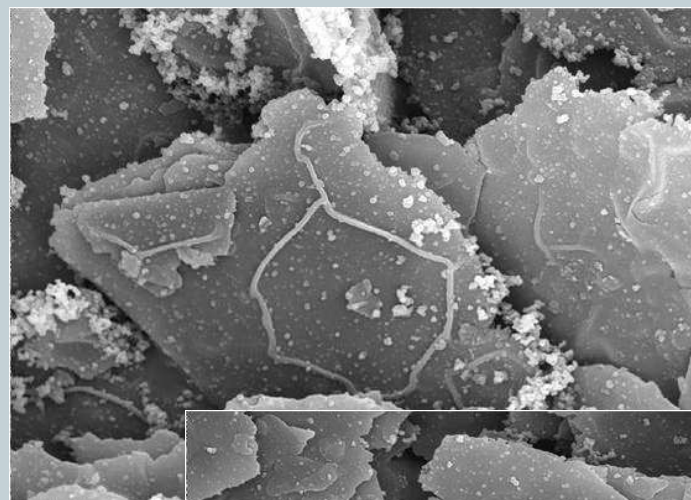
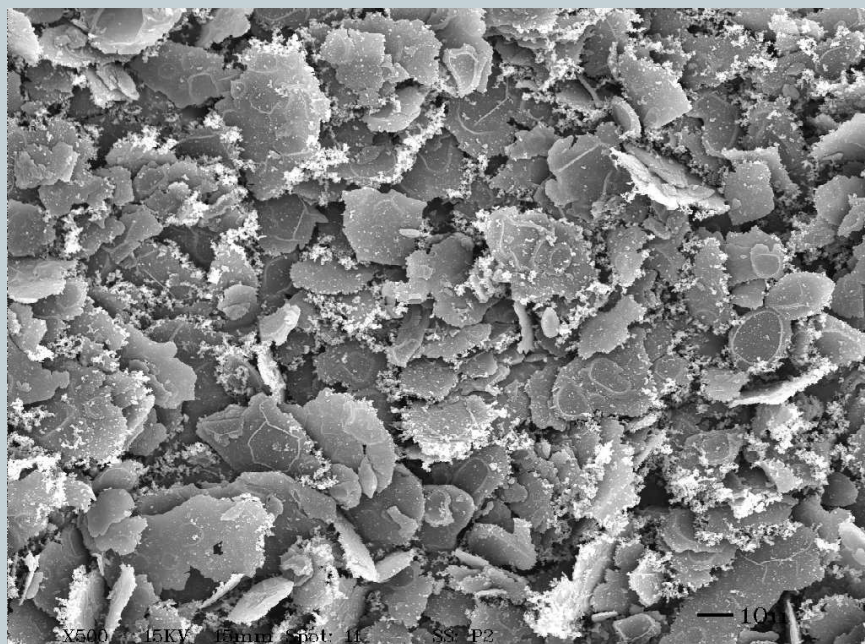


SEM Continued

7

PPy (no Catechol)

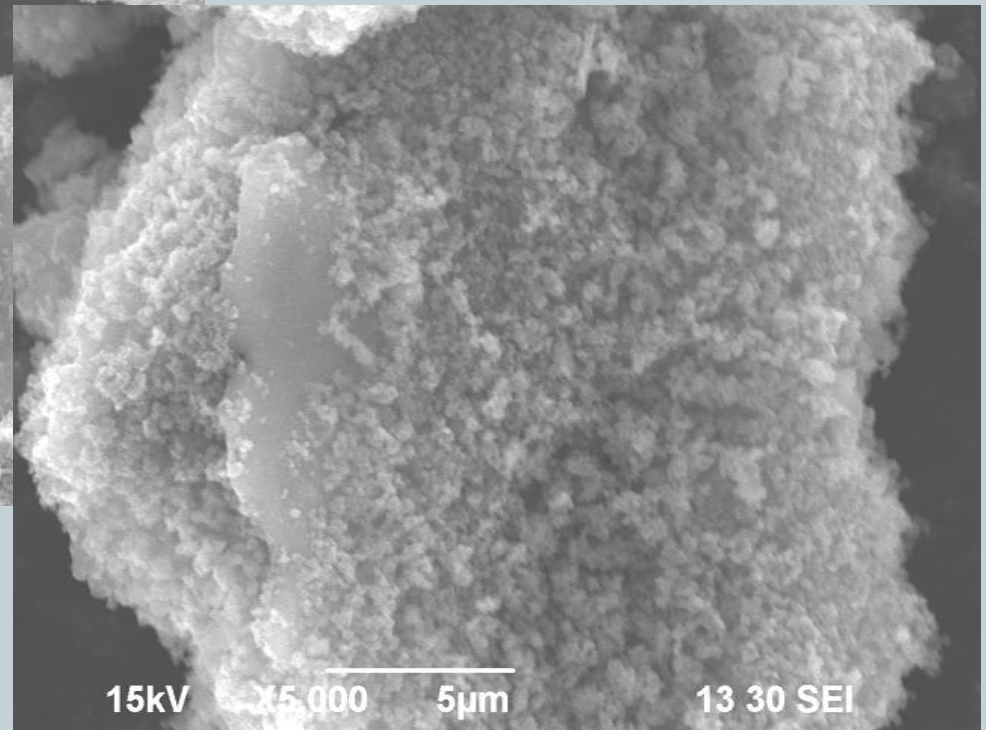
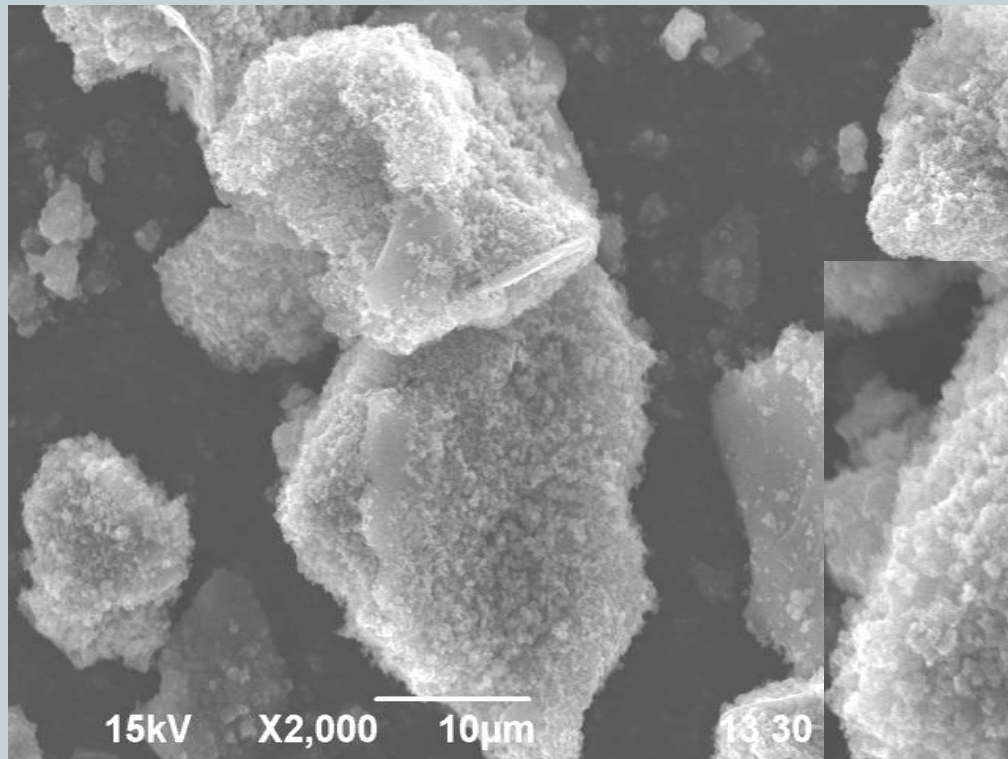
Ex #2



SEM (No Gold)

Ex #1

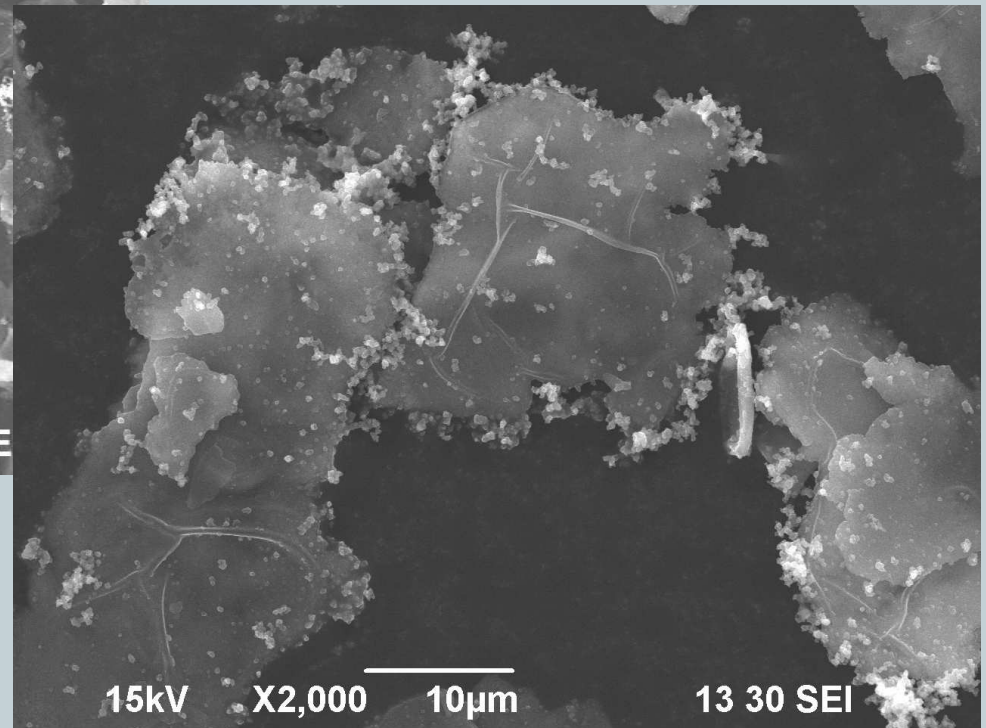
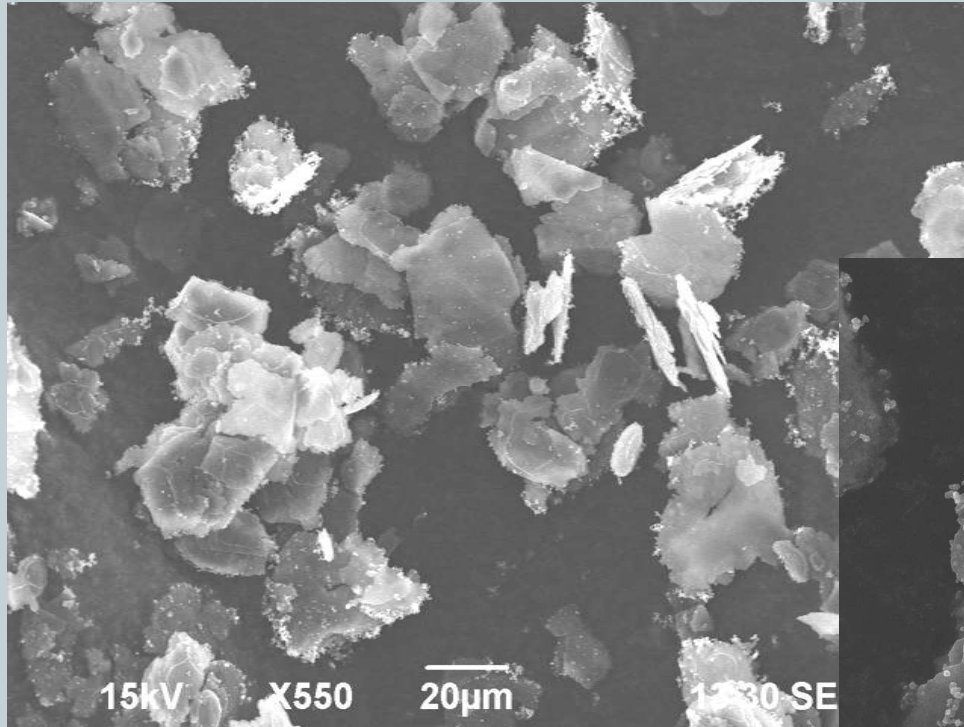
8



SEM (No Gold)

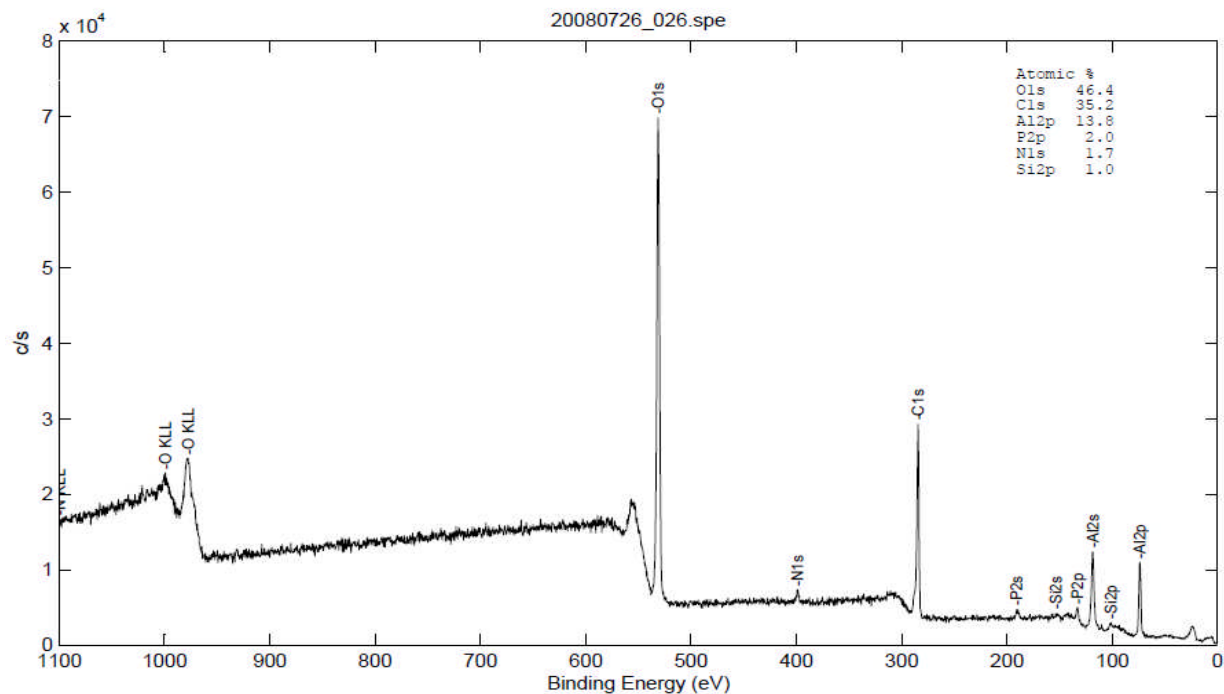
Ex #2

9



XPS

As-Received Al Flake



From MSDS of Flake
39.00 % aluminum

26.00% aluminum oxide

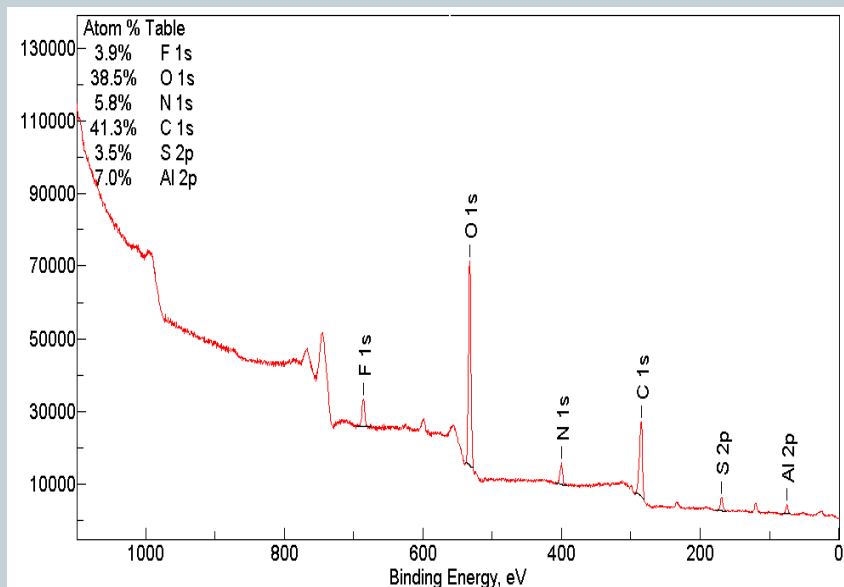
35.00% 1-methoxy-2-
propanol

Atomic %	
O1s	46.4
C1s	35.2
Al2p	13.8
P2p	2.0
N1s	1.7
Si2p	1.0

From XPS, it appears the coatings are ~10-20 nm thick

11

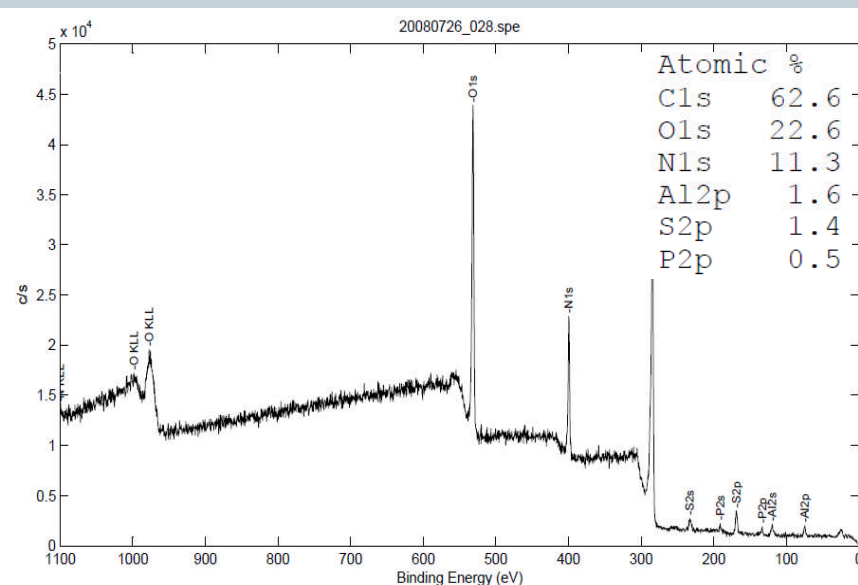
Polypyrrole/Al Flake from Experiment #1



S/N (Dopant Level)
S/N = ~3/5
3 dopant ions per 5
pyrrole units

C/N (Polymer)
C/N = ~7/1
4/1 if polypyrrole

Polypyrrole/Al Flake from Experiment #2



S/N (Dopant Level)
S/N = ~1/11
1 dopant ions per 11
pyrrole units

C/N (Polymer)
C/N = ~5/1
4/1 if polypyrrole

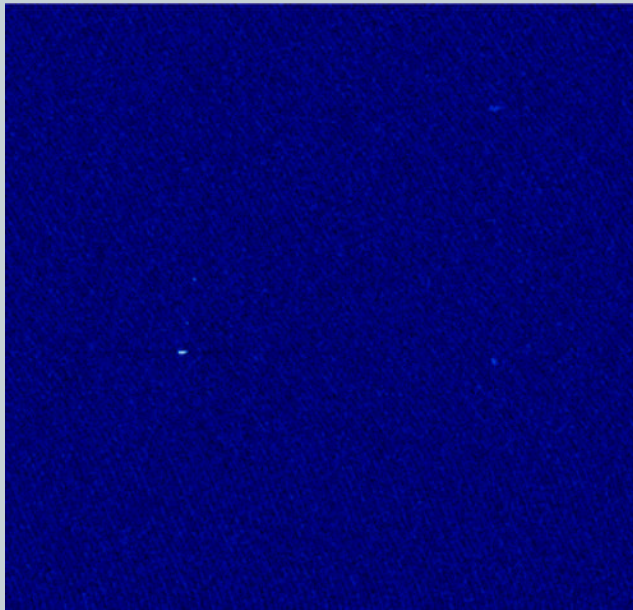
Conductive AFM

12

As-Received Flake

**Polypyrrole/AL Flake
Ex #1**

Current Image



$$\sigma_{\text{ave}} = 1.6 \text{ S/cm}$$

Scan Size 2.5 x 2.5 μm

Coating Formulation and Assessment

13

Formulations of Polypyrrole/Flakes

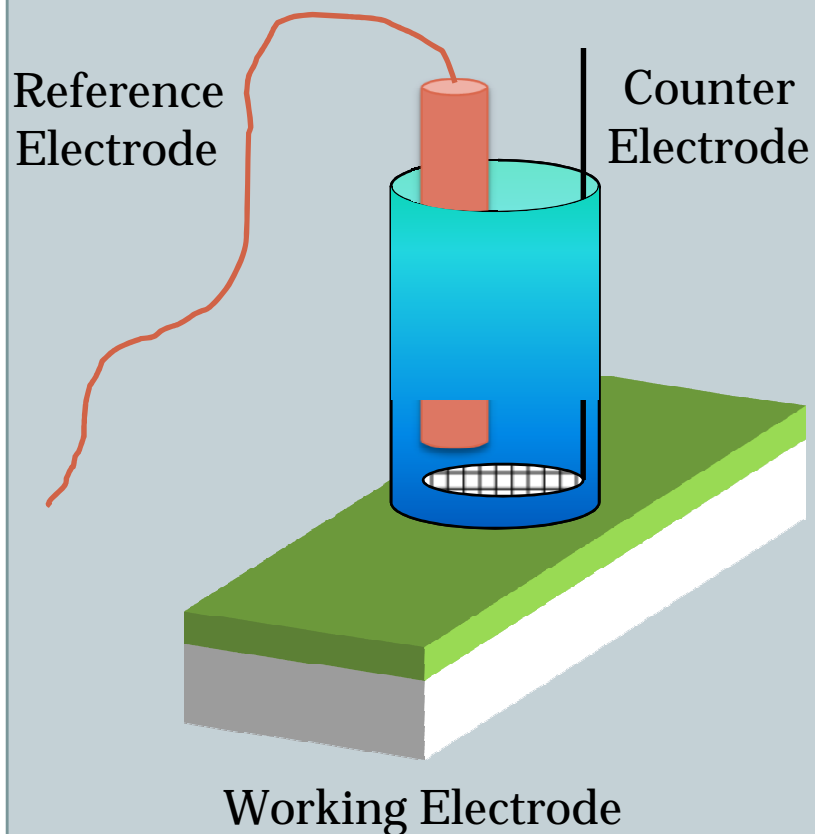
- Formulations prepared at various PVCs of coated and uncoated flakes and were combined with:
 - Epikure 3175 (aluminum) or Epikure 3115 (mica)
 - Epon Resin 828
 - Methyl Isobutyl Ketone (MiBK)

Al 2024-T3 panel application of formulation

- Coatings were applied to sanded and degreased 3" x 6" Al 2024-T3 panels using a 3" drawdown bar at 8 mils
- Panels were allowed to flash off and were then placed in an oven to fully cure

Electrochemical Impedance Spectroscopy

14



$$V = IR \text{ (DC)}$$

$$V = IZ \text{ (AC)}$$

Apply a small sinusoidal potential (~5 to 10 mV) to the open circuit potential at varying frequencies

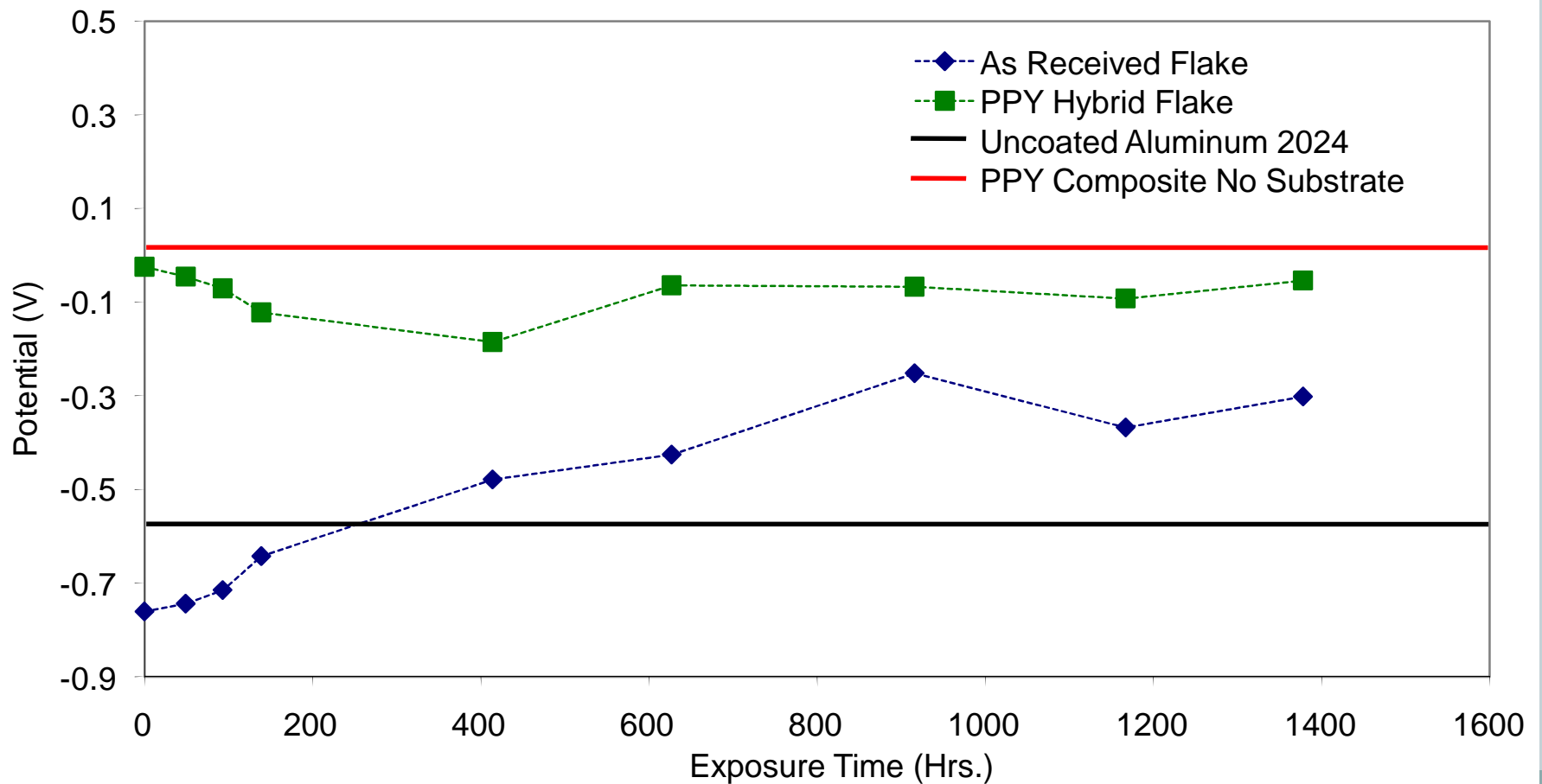
Measure phase lag (V- I) and current for varying applied frequencies

Presented usually as either a Bode (log modulus vs. log frequency) or a Nyquist plot (Z' vs. Z'')

Open Circuit Potentials

Al 2024-T3

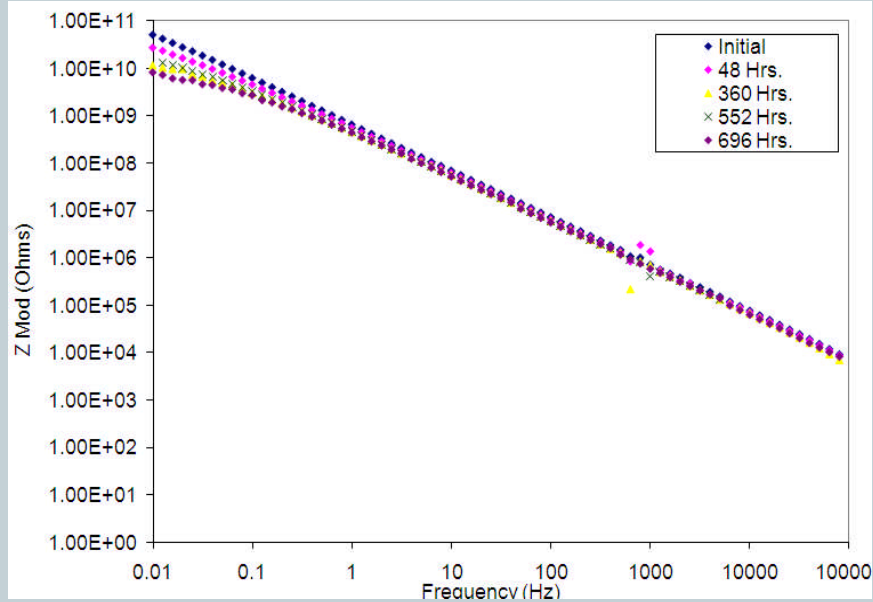
15



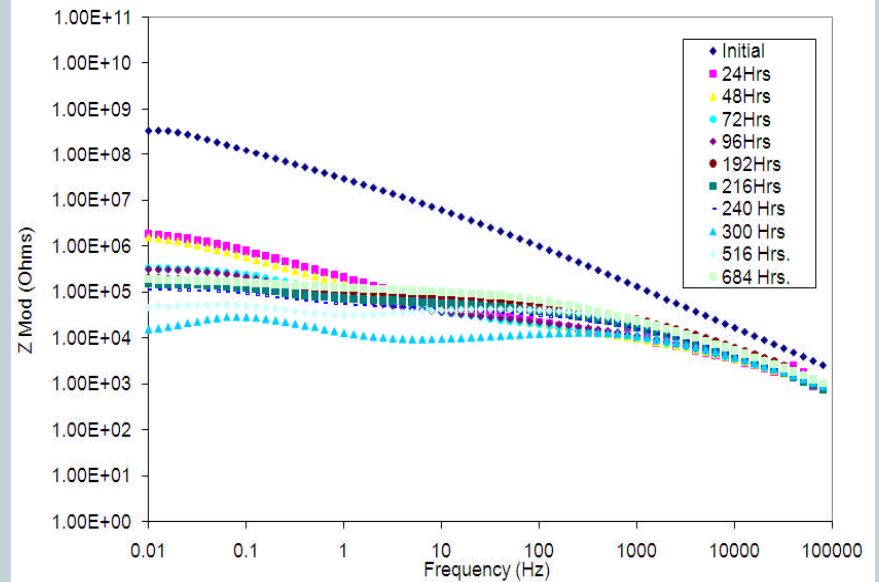
25% PVC—Aluminum

16

As-Received Flake

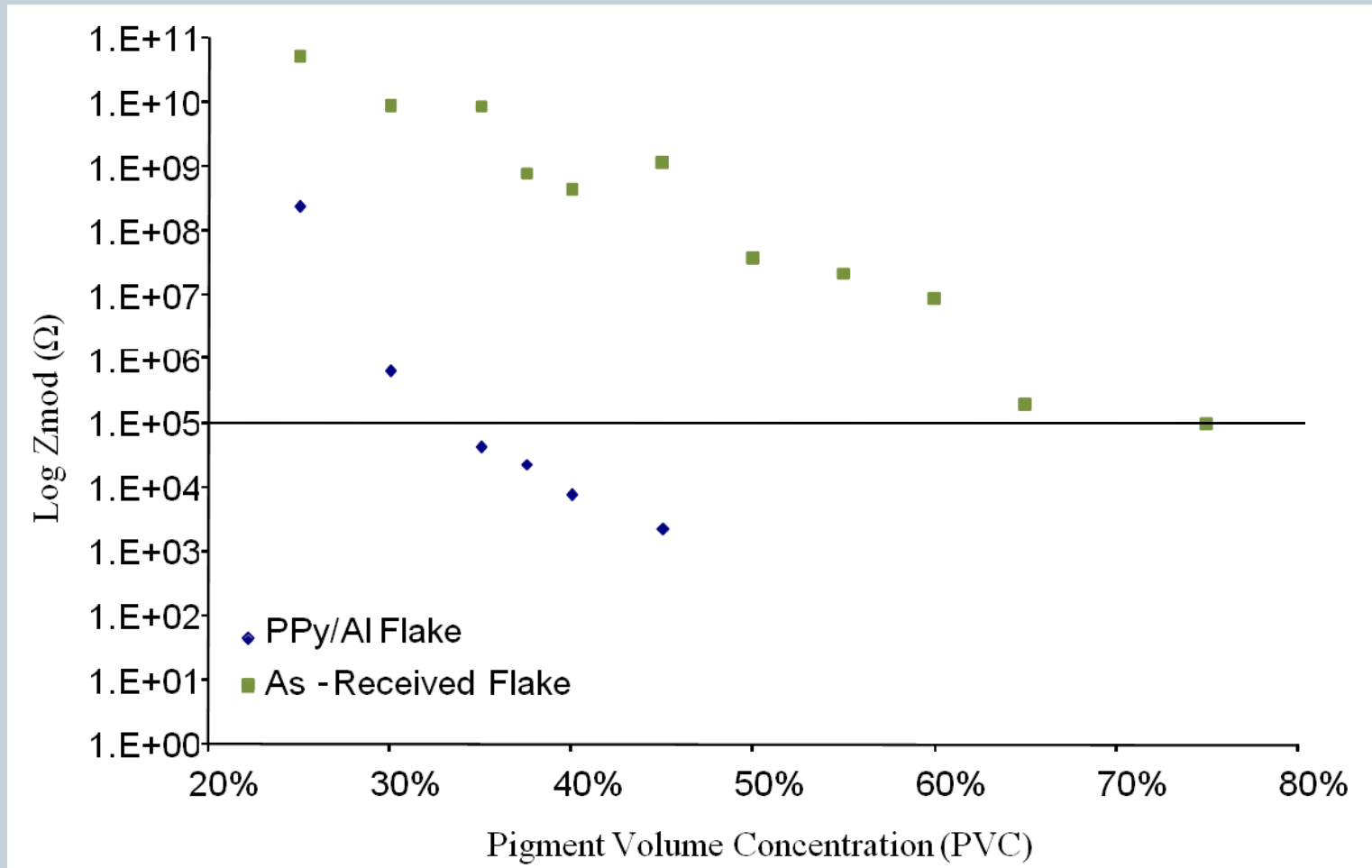


Polypyrrole Aluminum Flake



Impedance and PVC---Aluminum Flake

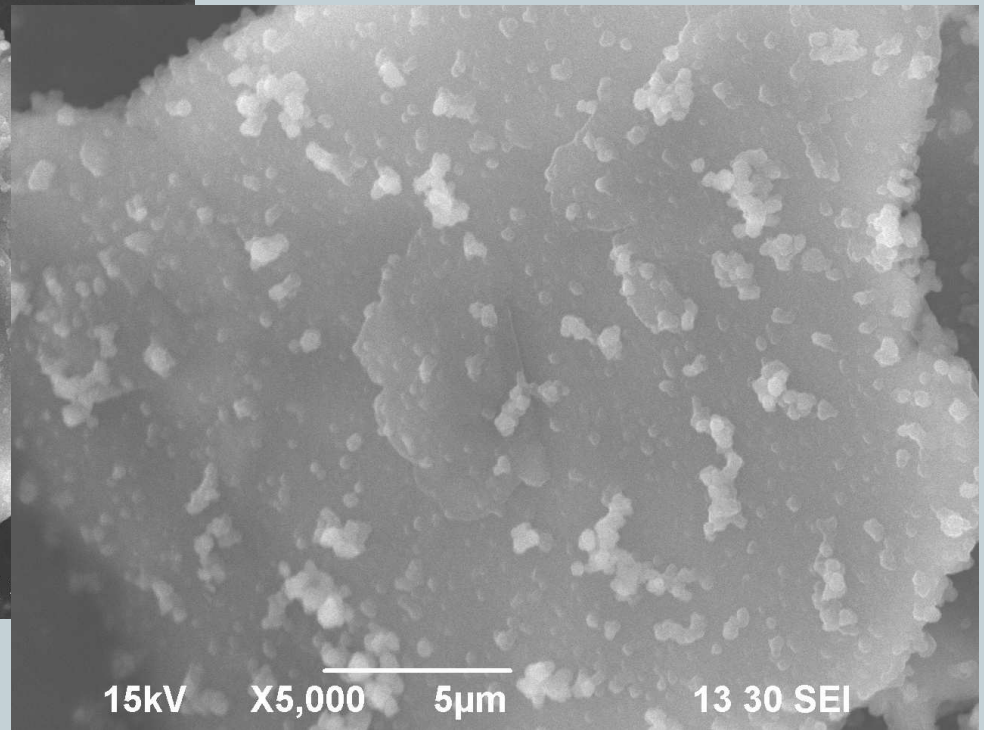
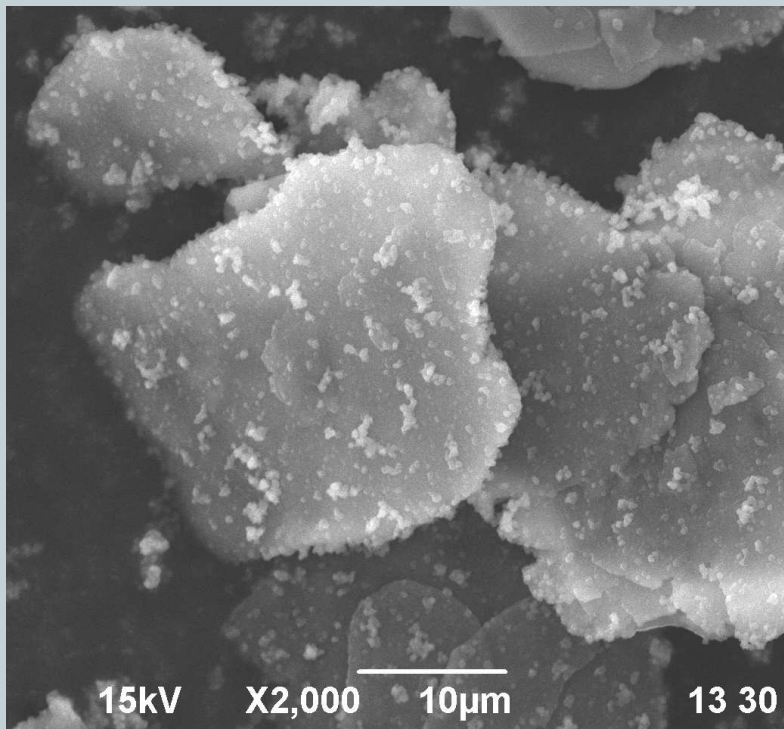
17



New Directions

18

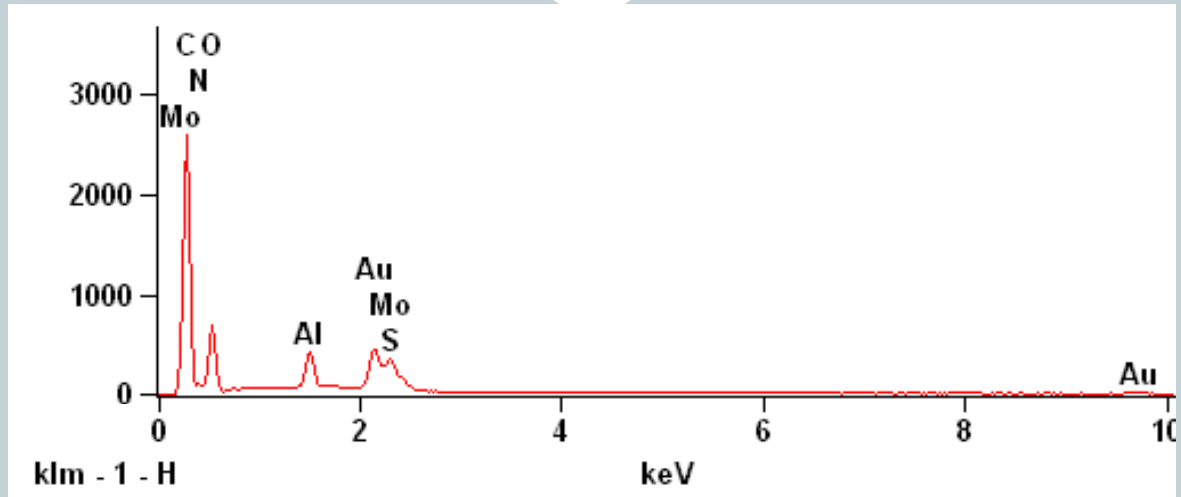
- Incorporation of corrosion inhibiting anions.



Molybdate

From EDX

19



Atom %

C	N	O	Al	S	Mo
76.04	8.42	14.19	0.76	0.05	0.54

Atom % Error ($\pm 3\sigma$)

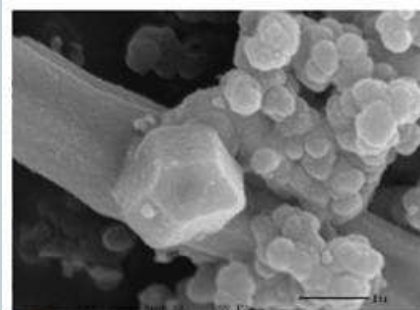
C	N	O	Al	S	Mo
1.67	7.10	1.46	0.07	0.20	.16

Photosynthesis of Polypyrrole

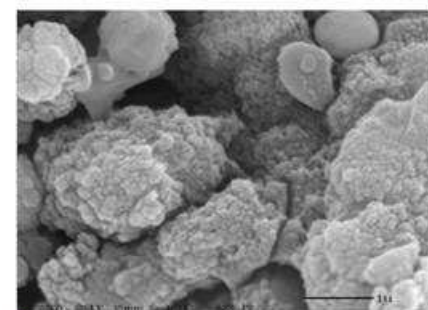
20

Part 2: Photo-chemical polymerization reactions (UV light)

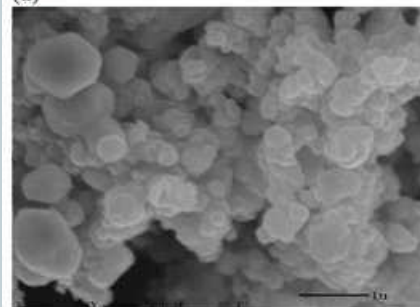
Label	Monomer	Oxidant	Pyrrole:Oxidant	Pyrrole:SDS	Pyrrole:pTSA
PPy-5	Pyrrole	AgNO ₃	1:1		
PPy-6	Pyrrole	AgNO ₃	1:1	4:1	
PPy-7	Pyrrole	AgNO ₃	1:1		4:1
PPy-8	Pyrrole	AgNO ₃	1:1	4:1	4:1



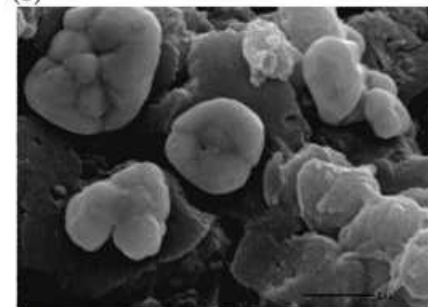
(a)



(b)

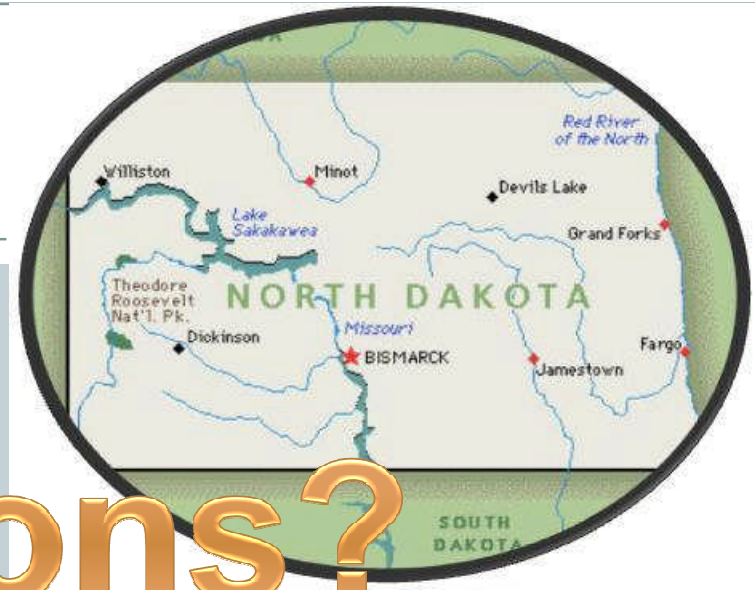


(c)



(d)

Polypyrrole Photo- chemically synthesized (a) without surfactant (PPy-5),
(b) SDS as surfactant (PPy-6), (c) pTSA as surfactant (PPy-7),
and (d) both SDS and pTSA (PPy-8)



Questions?



<http://dustydavis.com>; <http://images.politico.com>; <http://www.terrageria.com/>; <http://farm1.static.flickr.com>